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103005

DEPARTMENT OF THE ARMY
Fort Worth District, Corps of Engineers
P.O. Box 17300 (819 Taylor Street)
Fort Worth, Texas 76102-0300

Reply to
Attention of:

CESWF-PM-J

December 21, 2001

Ms. Annie Jarabek
U.S. Environmental Protection Agency
Catawba Building – Room 320
3210 Highway 54
Research Triangle Park, NC 27709

Subject: Perchlorate Data in Fish and Plants

Dear Ms. Jarabek:

This is in reference to the U.S. Environmental Protection Agency's risk assessment of perchlorate in drinking water. I understand that you are participating in this effort, and that you are a point of contact for this work.

As you may know, the U.S. Army Corps of Engineers is studying the potential of human and environmental exposure to perchlorate in the Bosque River and Leon River watersheds in Texas. As part of our study, we have been generating some data concerning perchlorate levels in fish and plants that occur in our study area. I thought that you might be interested in including our data in your risk assessment deliberations, so I am submitting the information that we have generated to date for your reference and use (see enclosures). Additional project information, including surface water quality data, may be found on our web site at www.swf.usace.army.mil/links/ppmd/perchlorate/index.html.

The data that we have generated so far is incomplete and uninterpreted, as our study is still in its early stages. Even so, my understanding is that data of this type is scarce, and that you probably would be interested in it even though it is in its "raw" form. I am enclosing the tables of data that our experts (The Institute of Environmental and Human Health at Texas Tech University) have developed so far.

If you have any questions concerning this data and how it was generated, please contact Dr. Phil Smith at 806-786-6908 (cell). During the period of 22 December 2001 through 3 January 2002, Dr. Smith may be reached at 270-443-3491. After January 3rd, you may contact Dr. Smith at the Institute at 806-885-0316, or Dr. Todd Anderson at 806-885-4567.

Sincerely,

Brian J. Condike
Project Manager

Cc: Perchlorate team

Encls:

Fish Head Data Table 1
Fish Fillet Data Table 2
Fish Fillet Data Table 3
Fish Head vs. Fish Fillet Data
Sediment Data
Plant Data

Table 1. Preliminary data on perchlorate concentrations in tissues from aquatic organisms within the Lake Waco and Lake Belton watersheds. Perchlorate concentrations are in ng/g (ppb) expressed based on tissue dry weight. Data represent the results of analyses of individual tissues (heads) with the number of analyses indicated parenthetically. Respective wet weight concentrations are presented in brackets. Samples were colleted in May, 2001 from areas previously identified through water quality analyses as having received perchlorate.

South Bosque at Indian Trail					
Suckers (4)	2030 [930]	Catfish(3)	1360 [630]	Largemouth Bass (1)	600 [280]
	1940 [890]		1010 [470]		
	2110 [970]		1850 [850]		
	2290 [1050]				
Harris Creek at Highway 317					
Sunfish (4)	740 [340]	Catfish (4)	730 [350]	Largemouth Bass (1)	ND
	890 [410]		190 [90]		
	ND		290 [140]		
	ND		270 [130]		
Harris Creek at Highway 84					
Sunfish (4)	710 [340]				
	360 [170]				
	1060 [500]				
	690 [330]				
Station Creek at Highway 107					
Sunfish (4)	ND				
	540 [240]				
	290 [130]				
	2730 [1230]				

ND = not detected by the analytical procedure [detection limit in dry tissue = 100 ppb]

Table 2. Preliminary data on perchlorate concentrations in tissues from aquatic organisms within the Lake Waco and Lake Belton watersheds. Perchlorate concentrations are in ng/g (ppb) expressed based on tissue dry weight. Data represent the results of analyses of individual tissues (fillets), except where indicated, with the number of analyses indicated parenthetically. Respective wet weight concentrations are presented in brackets. Samples were colleted in May, 2001 from areas previously identified through water quality analyses as having received perchlorate.

Harris Creek at Highway 317							
	Sunfish (4)	ND	Catfish (4)	TRACE	Shrimp* (1)	ND	Minnow* (1) ND**
		ND		ND			
		ND		50 [30]			
		ND		120 [60]			
Harris Creek at Oglesby Road							
	Minnow* (1)	ND**					
Harris Creek at Highway 84							
	Mosquitofish (1)	ND					
South Bosque at Indian Trail							
	Minnow* (3)	ND					
		ND					
		ND					
Station Creek at Highway 107							
	Sunfish (4)	70 [40]					
		ND					
		60 [30]					
		ND					

ND = not detected by the analytical procedure [detection limit in dry tissue = 50 ppb].
TRACE = perchlorate was detected, but the perchlorate concentration in the extract was below the limit of quantitation (2.5 ppb).
*The whole body was extracted for analysis.
**Composite sample.

Table 3. Perchlorate concentrations in tissues from aquatic organisms within the Lake Waco and Lake Belton watersheds. Perchlorate concentrations are in ng/g (ppb) expressed based on tissue wet weight. Data represent the results of analyses of individual tissues (fillets), except where indicated, with the number of analyses indicated parenthetically. Samples were colleted in August-September, 2001 from areas previously identified through water quality analyses as having received perchlorate.

Harris Creek at Highway 317						
	Green sunfish (2)	ND	Large mouth bass (4)	TRACE	Yellow bullhead (1)	ND
		ND		ND		
				ND		
				ND		
Harris Creek at Oglesby Road						
	Green sunfish (2)	ND	Yellow bullhead (1)	TRACE		
		ND				
South Bosque at Highway 84						
	Carp (2)	ND	Channel catfish (6)	ND	Flat head catfish (1)	ND
		ND		ND		
				ND		
				ND		
				ND		
				ND		
	Green sunfish (1)	ND	Large mouth bass (5)	690	Sunfish (2)	ND
				ND		ND
				ND		
				ND		
				ND		
	Sucker (1)	ND	White bass (1)	ND		
South Bosque at Indian Trail						
	Large mouth bass (16)	590 ND	Sunfish (6)	ND	Sucker (1)	ND

	ND	ND		ND
	ND	ND		ND
	ND	ND		ND
	ND	ND		ND
	ND	ND		ND
	ND	ND		
	ND	ND		

South Branch of South Bosque at Highway 317

Green sunfish (2)	260		
	ND		

Station Creek at Leon River

Channel catfish (4)	ND	Yellow bullhead (1)	ND
	ND		
	ND		
	260		

ND = not detected by the analytical procedure [detection limit in wet tissue = 170 ppb].
TRACE = perchlorate was detected, but the perchlorate concentration in the extract was below the limit of quantitation (2.5 ppb).

Table X. Perchlorate concentrations in tissues from catfish exposed to sodium perchlorate (100 ppm) in the laboratory over 5 days. Perchlorate concentrations are in ng/g (ppb) expressed based on tissue wet weight. Data represent the results of analyses of individual fish.

Sample	Fillet	Head
1807	7010	23250
1808	7720	23910
1809	5720	23570
1810	5770	27350
1811	5800	17420
1812	8410	25690
1813	5880	15470
1814	7970	18080
1815	6330	20520
1816	8060	24450
1817	6130	21070
1818	10200	45760
1819	8000	34460
1820	8430	32280
1821	7840	28620
Mean	7280	25460
SD	1320	7690

Distribution Ratio $[ClO_4^-]_{head} / [ClO_4^-]_{fillet} = 3.5$

Table 2. Perchlorate concentrations in sediment porewater within the Lake Waco and Lake Belton watersheds. Perchlorate concentrations are in ng/mL (ppb). Samples were collected in August-September, 2001 primarily from areas where fish samples were also collected. Collection dates are indicated parenthetically.

Harris Creek at Highway 317		
00234	ND	(090601)*
00235	ND	(090601)*
Harris Creek at Oglesby Road		
02244	ND	(090601)
Willow Creek at Highway 317		
02304	ND	(090601)
02321	ND	(090601)
North Branch of South Bosque at Highway 317		
02300	ND	(090701)
02320	ND	(090701)
South Bosque at Indian Trail		
00478	ND	(082901)*
00479	ND	(082901)*
South Bosque at Highway 84		
00468	ND	(082801)*
00448	ND	(082801)*
00519	ND	(082801)*
00420	ND	(082801)*
00518	ND	(082801)*
Station Creek at Leon River		
00269	ND	(090601)
00268	ND	(090601)
02243	ND	(090701)*
02272	ND	(090701)*

*Date of fish collection.
ND = not detected by the analytical procedure [detection limit = 2 ppb].
TRACE = perchlorate was detected, but the perchlorate concentration was below the limit of quantitation (2.5 ppb).

Preliminary Results on the Fate of Perchlorate in Near Surface Sediments in the Lake Waco/Belton Watershed

Introduction

The fate of perchlorate in near surface sediments is of interest. Perchlorate in sediment porewater is likely to be less subject to drastic concentration changes as well as being a better indicator of the available pool for plant uptake. In addition, microbial transformations of perchlorate are likely to take place in the sediment rather than bulk stream water due to the typical oxygen concentrations above 1 ppm. In order to determine the concentration of perchlorate and the potential for microbial transformation of perchlorate, dialysis samplers were deployed at a number of locations surrounding the McGregor facility.

Peepers are diffusion chambers, which can be used to determine the vertical distribution of most soluble constituents in soil pore water. They have been used to study the distribution of common anions and cations including most metals, dissolved organic carbon, toxic organics, and many other geochemical parameters. The chambers allow discrete vertical distribution profiles that are particularly useful in soils or sediments which are highly stratified over a short distance or in which there are rapid changes in redox zones over small distances. One common type of system that exhibits these qualities and has been investigated using this technique is wetlands. Peepers have been found to be superior to other pore water collection techniques in these systems.

Method

A typical chamber is 60 cm long and capable of holding 11 ml of water every 2 cm. The water wells were separated from the soil matrix by two membranes, one 8 μm and the other 0.45 μm. The chambers are inserted into a saturated medium to the desired depth and allowed to equilibrate for a given period of time 2-4 weeks. After the chambers have had time to equilibrate with the surrounding pore water the chambers are removed and sampled for the chemical species of concern. The sampling is normally accomplished by removing the water in each well by syringe. This can be conducted under a nitrogen blanket to prevent changes due to oxidation reactions. Modifications can be made to suite particular site requirements, needed vertical resolution, or equilibration times.

Three peepers were inserted on May 14, 2001. Locations sampled included the North Branch of the South Bosque at Highway 317, the South Branch of the South Bosque at Mother Neff Loop, and Harris Creek at Highway 84. Peepers were retrieved May 28, 2001. Samples were analyzed for a variety of anions including perchlorate, sulfate, nitrate, nitrite, phosphorous, and chloride. Bulk water samples and some plant samples were taken at the time of insertion.

Results

At two of the locations sampled (S. Bosque at Highway 317 and Harris Creek at Highway 84) there were detectable concentrations of perchlorate in the sediment profile. No perchlorate was found in sediments at the third location. Table 1 lists the perchlorate

concentration in the bulk water at the time the peepers were inserted. In addition, plant samples were also collected at two of the locations (dry weight perchlorate concentrations are listed). Figure 1 presents the anion profile below the sediment water interface at S. Bosque at 317. Perchlorate concentrations ranged from 4 to 15 ppb with no apparent trend. Little nitrate was present and there was some indication of sulfate reduction in porewater near the sediment water interface.

Figure 2 presents the anion concentration in sediment in Harris Creek at Highway 84. Higher concentrations of perchlorate, although still low (25- to <4), were identified in these sediments. Of interest are the rapidly decreasing concentrations of perchlorate with depth. Concentrations of perchlorate, NO_3, and SO_4 are fairly stable near the sediment water interface (depths of 3 and 5 cm). Perchlorate rapidly diminishes at lower depths coinciding with the use of NO_3 as an electron acceptor. Some sulfate reduction also appears to occur with full reduction of these electron acceptors at depths of 9 cm and greater.

No perchlorate was found in sediments North of Mother Neff Loop on the S. Bosque South Branch.

Location	Bulk Water Perchlorate Concentration (µg/l)	Plant Species	Concentration of Perchlorate in Plant mg of ClO_4/kg dry plant
317	440	Algae	ND
84	49	Not Collected	
S. Bosque at Mother Neff Rd.	ND	Algae	5.52

Figure 1. Concentration of Anions in Pore Water Sediments Upstream of Highway 317 on N. Bosque.

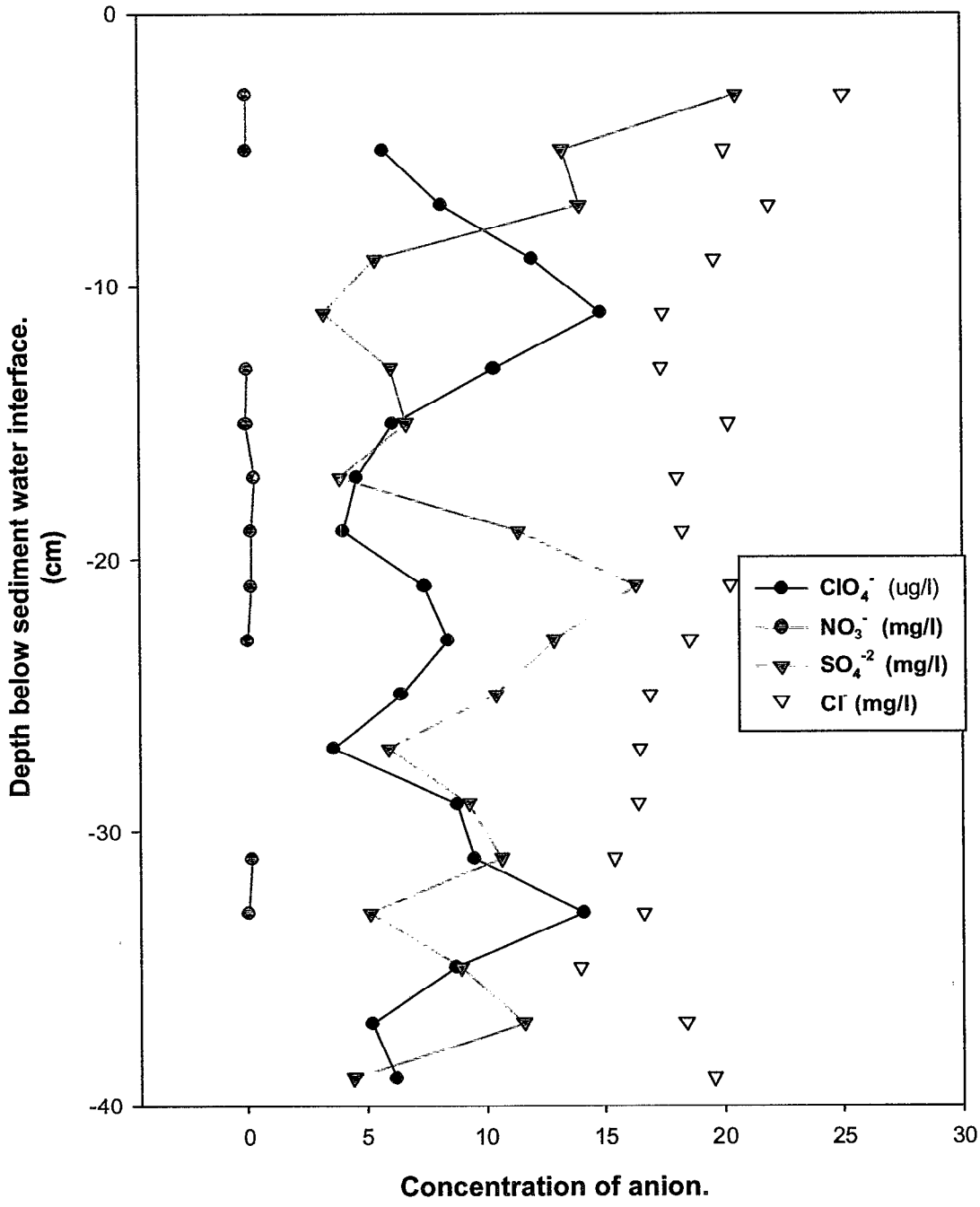
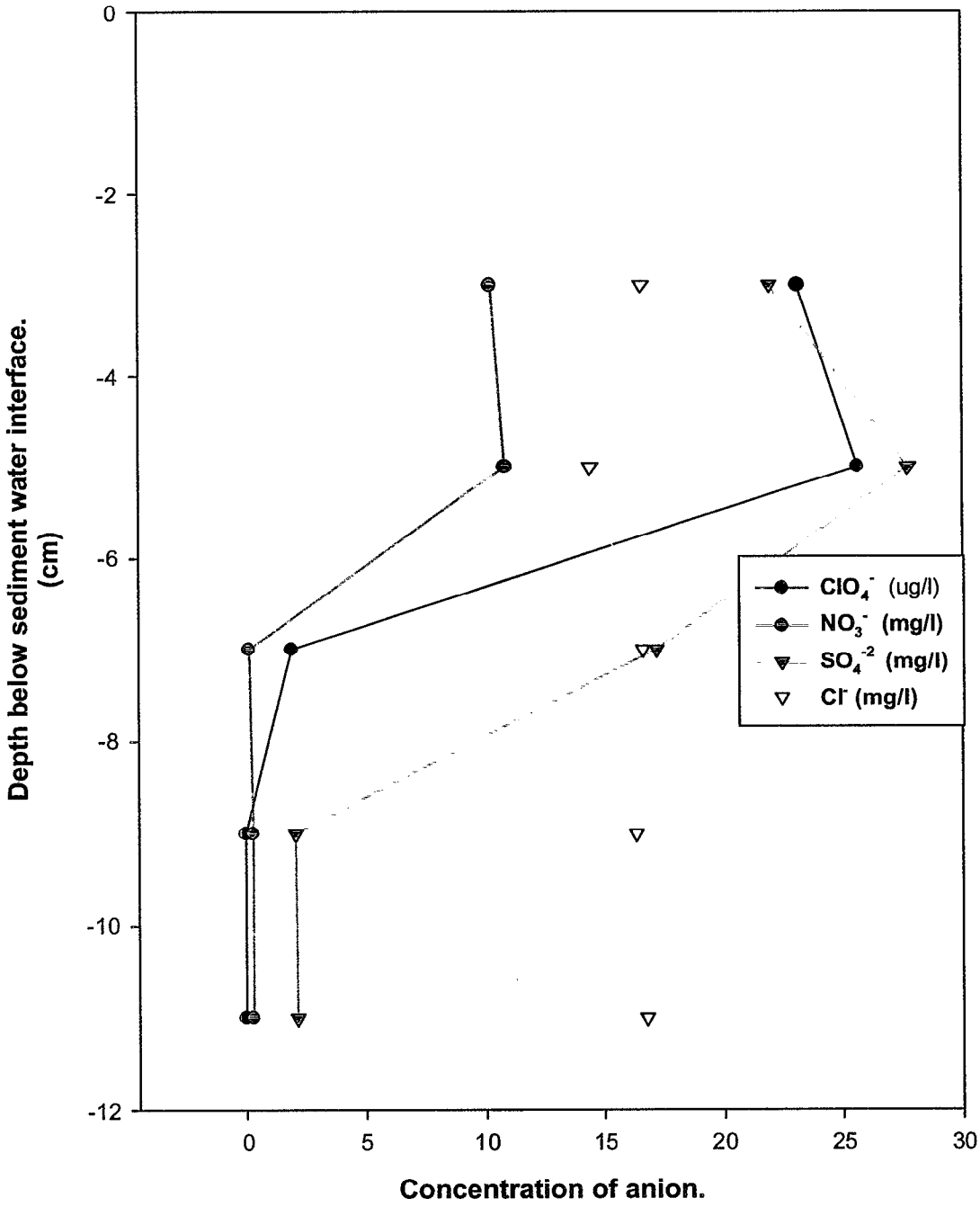
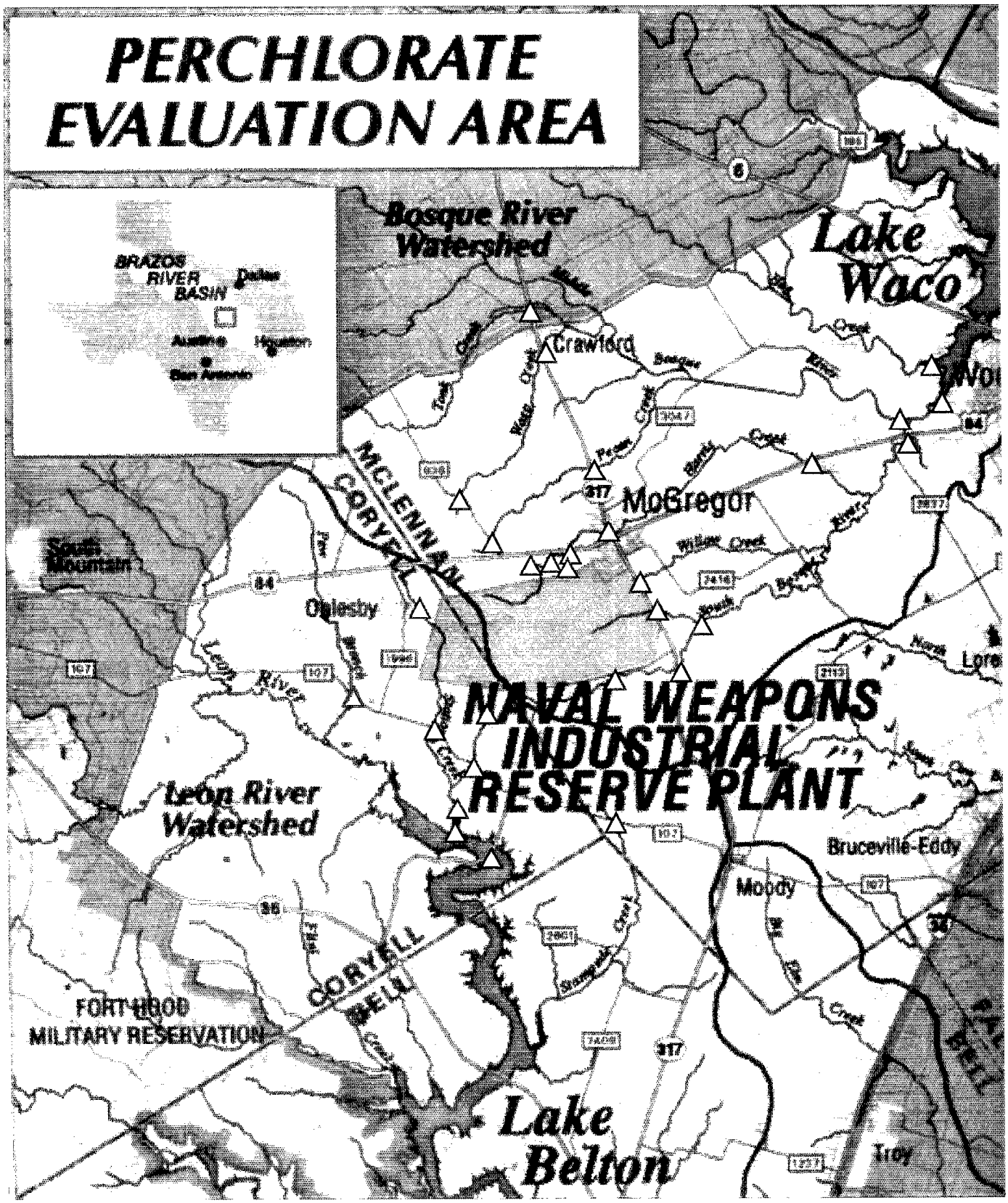


Figure 2. Concentration of Anions in Pore Water Sediments Upstream of Highway 84 on Harris Creek.




PERCHLORATE EVALUATION AREA
BRAZOS RIVER BASIN
Dallas
Austin
Houston
San Antonio
Bosque River Watershed
Lake Waco
Crawford
McGregor
MCLENNAN
CORYELL
South Mountain
Oglesby
NAVAL WEAPONS INDUSTRIAL RESERVE PLANT
Leon River Watershed
Bruceville-Eddy
Moody
CORYELL
BELL
FORT HOOD MILITARY RESERVATION
Lake Belton
Troy